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(54) Polybutadiene and process for preparing the same.

(57) A polybutadiene having an average 1,2-bond content of 18 to 32% by mole, a branched polymer chain content of 60% by weight or more and a Mooney viscosity at 100°C of 40 to 90, the viscosity of a 5% by weight concentration solution of this polybutadiene in styrene at 25°C being 60 to 90 cps, and a process for preparing the polybutadiene comprising starting the polymerization of 1,3-butadiene in an inert hydrocarbon solvent in the presence of a Lewis basic compound and an organolithium compound, the latter compound being in an amount of 0.5 to 3 millimoles per 100 g of 1,3-butadiene, at a temperature selected from the range of 30 to 80°C, carrying out the polymerization by controlling the temperature so that the temperature at the end of polymerization may be 5 to 40°C higher than the temperature at the start of polymerization, and adding to the resulting polymer solution a polyfunctional halogen compound in an amount of 0.6 to 1 equivalent per equivalent of the organolithium compound to further react the polymer with the polyfunctional halogen compound.

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## POLYBUTADIENE AND PROCESS FOR PREPARING THE SAME

1           This invention relates to polybutadienes,  
particularly to a novel polybutadiene which is suitable  
for improving various properties such as impact strength,  
luster, etc., of resinous polymers such as, typically,  
5   styrene polymer (PS) and polymethyl methacrylate (PMMA),  
and a process for preparing such polybutadiene.

          Recently, synthetic resins such as PS and PMMA  
are used in great quantities in many fields of industry and  
for various purposes such as the manufacture of parts of  
10   automobiles, household electric appliances, etc., and  
accordingly the improvements of their mechanical pro-  
perties and visual appearance characteristics such as  
luster are strongly required. In the case of PMMA, for  
instance, it is required to improve both impact strength  
15   and transparency at the same time, and in the case of PS,  
simultaneous improvement of impact strength and surface  
luster is required.

          It has been known to mix butadiene rubber or to  
graft polymerize methyl methacrylate monomer or styrene  
20   monomer in the presence of butadiene rubber for improving  
the impact strength of said resinous polymers.

          However, use of commercially available poly-  
butadiene with a high cis content (so-called high-cis BR)  
as said butadiene rubber cannot provide a satisfactory  
25   impact strength-improving effect and, in some cases,

1 the obtained resin product is tinted. Also, the impact  
strength may rather be lowered due to presence of gel  
substance. On the other hand, use of commercial poly-  
butadiene with a relatively high trans content (so-called  
5 low-cis BR) synthesized with a lithium type polymerization  
initiator can keep the gel content relatively low and  
also provides a significant improvement of impact strength,  
but problems exist in this case, too. It is necessary  
to increase the amount of polybutadiene used or to increase  
10 the average molecular weight of polybutadiene for achieving  
a further improvement of impact strength, but this invites  
a deterioration of luster or transparency of the resin  
product. Thus, it has been impossible for either of said  
types of polybutadiene to improve both impact strength  
15 and appearance characteristics of resinous polymers at the  
same time.

In view of the above, the present inventors  
have pursued further studies for developing a new type  
of polybutadiene which is effective for improving both  
20 impact resistance and appearance characteristics of  
resinous polymers as mentioned above, and as a result,  
have succeeded in developing a novel polybutadiene having  
a specific structure and capable of achieving said object.  
The present invention has been realized on the basis of  
25 such achievement.

Thus, the present invention provides a novel  
polybutadiene having branched polymer chains obtained by  
polymerizing 1,3-butadiene in the presence of an organo-

1 lithium compound and a Lewis basic compound and further  
reacting the produced polymer with a polyfunctional  
halogen compound, said polybutadiene being characterized  
in that the average 1,2-bond content is 18 to 32% by mole,  
5 that the branched polymer chain content is 60% by weight  
or more, that the Mooney viscosity at 100°C is 40 to 90,  
and that the viscosity of a 5% by weight concentration  
solution of polybutadiene in styrene at 25°C is 60 to 90 cps.  
Such polybutadiene can be produced by starting polymeri-  
10 zation of 1,3-butadiene in an inert hydrocarbon solvent  
in the presence of a Lewis basic compound and an organo-  
lithium compound, the latter compound being used in an  
amount of 0.5 to 3 millimoles per 100 g of 1,3-butadiene,  
at a temperature selected from the range from 30 to 80°C,  
15 carrying out the polymerization under temperature control  
such that the temperature at the end of polymerization  
may be 5 to 40°C higher than the temperature at the start  
of polymerization, and adding to the obtained polymer  
solution a polyfunctional halogen compound in an amount  
20 of 0.6 to 1 equivalent per equivalent of organolithium  
compound for further reacting said polymer.

As the organolithium compound used in the  
preparation of said polybutadiene, there can be employed  
hydrocarbon compounds containing lithium atom such as n-  
25 propyllithium, isopropyllithium, n-butyllithium, sec-  
butyllithium, t-butyllithium, n-pentyllithium and the like  
which are the polymerization initiators for the so-called  
"living anionic polymerization". Such compounds are

1 usually used in an amount of 0.5 to 3 millimoles per  
100 g of 1,3-butadiene.

If the amount of organolithium compound used  
is less than 0.5 millimole, the viscosity of the poly-  
5 merization system rises to not only cause difficulties in  
the removal of reaction heat, control of reaction temper-  
ature and recovery of polybutadiene but also result in  
an excessively high molecular weight of the produced  
polybutadiene. On the other hand, use of said organo-  
10 lithium compound in excess of 3 millimoles results in a  
too low molecular weight of the produced polybutadiene.

As the Lewis basic compound, there can be used  
ethers such as diethyl ether, dibutyl ether, tetrahydrofuran,  
ethylene glycol dimethyl ether, ethylene glycol dibutyl  
15 ether, diethylene glycol dimethyl ether, diethylene  
glycol dibutyl ether and the like or tertiary amines such  
as triethylamine, tributylamine, N,N,N',N'-tetramethyl-  
ethylenediamine and the like, these compounds being usable  
either solely or as a mixture of two or more of them.

20 The average 1,2-bond content of polybutadiene  
according to this invention is defined to be in the range  
of 18 to 32% by mole, preferably 20 to 30% by mole. If  
said average 1,2-bond content is below the above-defined  
range, the resulting resin product proves poor in luster  
25 and transparency, while if said content exceeds said range,  
the resin product becomes low in impact strength.

The desired control of 1,2-bond content can be  
effected by properly selecting the type and the amount of

1 Lewis basic compound used and incorporating it in the  
system at the time of polymerization of 1,3-butadiene.  
For instance, in case of using diethylene glycol dimethyl  
ether as said Lewis basic compound, the amount thereof  
5 used should be 0.05 to 0.15 mole per mole of organolithium  
compound.

It is desirable that the distribution of 1,2-bond  
content is oriented in the lengthwise direction of the  
polymer chain, and it is particularly preferable that  
10 the value of 1,2-bond content (% by mole) in the 10% length  
portion of the polymer chain from its polymerization  
starting end is 3 to 20% by mole higher than the value of  
1,2-bond content (% by mole) in the 10% length portion of  
the chain from its polymerization terminating end.

15 This polymerization reaction is carried out  
in an inert hydrocarbon solvent such as n-hexane, n-heptane,  
cyclohexane, benzene, toluene, xylene and the like.

Polymerization temperature is an important  
factor in the production of polybutadiene according to  
20 this invention, and it is desirable to control the poly-  
merization temperature such that the average temperature  
of the reaction system at a point before reaching 10%  
conversion may be 5 to 40°C lower than the average temper-  
ature of the reaction system at a point after reaching 90%  
25 conversion but before the end of the polymerization.

In more concrete terms, the polymerization is  
started at a temperature selected from the range from  
30 to 80°C, and by utilizing the polymerization reaction

1 heat or by supplying heat from the outside, the polymeriza-  
tion temperature being controlled such that the temperature  
at the end of the polymerization may be in the range of  
35 to 120°C and furthermore 5 to 40°C higher than the  
5 starting temperature of polymerization.

----- If the polymerization starting temperature is  
below 30°C, the polymerization reaction rate becomes  
inpractically low, while if the starting temperature is  
higher than 80°C, it becomes difficult to control the  
10 reaction temperature and also the molecular weight distribu-  
tion of the produced polybutadiene tends to change un-  
stably, and when, for instance, an impact-resistant poly-  
styrene resin is produced by using such polybutadiene  
as starting material, the resulting resin lacks quality  
15 stability and, in particular, proves poor in visual  
properties such as surface luster.

It is also desirable that the temperature at  
the end of polymerization reaction is high in view of  
economy in the industrial practice of the process, but if  
20 such temperature exceeds 120°C, it becomes difficult to  
control the average 1,2-bond content of produced poly-  
butadiene at the range of 18 to 32% by mole. This also  
leads to a disadvantage of necessitating a large amount of  
a Lewis basic compound. Further, the control of molecular  
25 weight distribution of polybutadiene becomes difficult,  
and the resin produced by using such polybutadiene is  
deteriorated in visual appearance properties.

The polybutadiene of this invention is

- 1 characterized by containing 60% by weight or more, preferably 80% by weight or more of branched polymer chains formed by reacting a polyfunctional halogen compound with the active polymerization terminal of a polymer
- 5 obtained from said polymerization reaction. If the content of said branched polymer chain is less than 60% by weight, the viscosity of the system becomes exceedingly high in producing a resin by mixing a monomer such as styrene or methyl methacrylate with the polybutadiene.
- 10 Also, the produced resin proves to be poor in stability and reproducibility of mechanical properties.

The content of branched polymer chains can be controlled by adjusting the quantity ratio of the polyfunctional halogen compound to the organolithium compound

15 used as a polymerization initiator. For instance, one or a mixture of two or more of polyfunctional halogen compounds such as dimethylsilicon dichloride, monomethylsilicon trichloride, silicon tetrachloride, tin tetrachloride, germanium tetrachloride and the like is used

20 in an amount of 0.6 to 1 equivalent per equivalent of organolithium compound, and it is added to the polymer solution obtained from said polymerization and reacted with the active polymerization terminal of the polymer.

The molecular weight of polybutadiene according

25 to this invention should be such that the following conditions are met: the Mooney viscosity at 100°C is 40 to 90; and the viscosity of a 5% by weight concentration solution of polybutadiene in styrene at 25°C is 60 to

1 90 cps.

If the molecular weight is too small to fulfill these conditions, the produced resin proves low in impact strength or poor in stability and reproducibility of  
5 properties. On the other hand, if the molecular weight is too large to meet said conditions, the produced resin has poor appearance properties such as luster. Also, difficulties will be caused in stirring and mixing materials in an apparatus in the synthesis of a resin, making it  
10 unable to maintain the uniformness of the resin product quality.

The polybutadiene of this invention is further characterized by a favorable small value of cold flow and easy miscibility at the time of dissolution, owing to  
15 the fact that the values of Mooney viscosity (ML) and solution viscosity (SV) substantially satisfy the relation of  $0.7 \times ML \leq SV \leq 1.3 \times ML$ .

In use of the polybutadiene of this invention as a starting material for the production of resins,  
20 the viscosity of the system can be maintained in a range that enables homogeneous mixing operation in an ordinary stirring or mixing tank, so that the produced resin can be maintained uniform in qualities. This invention has also provided a great progress in the art in that it has  
25 realized simultaneous improvement of both visual appearance properties such as surface luster and mechanical properties such as impact strength of a resin, which has been quite difficult in the conventional techniques.

1           The present invention will be further illustrated  
below by way of the embodiments thereof.

Examples 1-3 & Comparative Examples 1-5

5           An autoclave having an internal volume of 10  
litres and equipped with a stirrer and a jacket had its  
interior atmosphere sufficiently replaced with dry  
nitrogen gas, and into this autoclave were fed 7 litres of  
dry cyclohexane, 1 kg of 1,3-butadiene and diethylene  
glycol dimethyl ether (varied in amount), with the internal  
10   temperature of the autoclave being adjusted at 40°C. Then  
n-butyllithium (varied in amount) was added to the mixture  
and the polymerization was started. After about 180-minute  
reaction under heating to approximately 60 to 70°C, tin  
tetrachloride (varied in amount) was added to continue  
15   the reaction for additional 30 minutes. To the resulting  
polymer solution was added 0.5 PHR (by weight) of 2,6-di-  
t-butyl-4-methylphenol as a stabilizer, and then the solvent  
was distilled off to obtain a polybutadiene.

20           The synthesis conditions and the structural  
analytical values of the produced polybutadienes in the  
respective examples are shown in Table 1. The poly-  
butadienes of Comparative Examples 3 to 5 are those  
synthesized at a fixed polymerization temperature of  
55°C.

25           The structural analysis of the produced poly-  
butadienes was made in the manner described below.

1 1,2-bond content

Infrared absorption spectrophotometry was used. The average 1,2-bond content was measured with the finally synthesized polybutadienes.

5 For the determination of distribution of 1,2-bond content along the polybutadiene chain, the polymerization solution was sampled out at given time intervals in the course of polymerization of polybutadiene and the polymerization conversion and 1,2-bond content of  
10 each sample were measured by calculating the 1,2-bond content in the portion where the polymerization conversion was less than 10% and in the portion where the polymerization conversion was 90 to 100%.

Mooney viscosity

15 A Mooney viscometer set at 100°C was used. After one-minute preheating and additional four-minute standing, the torque was read. (ML, 1+4, 100°C).

Content of branched polymer chains

Toyo Soda's HLC-802UR was used, selecting  
20 columns of  $10^3$ ,  $10^4$ ,  $10^6$  and  $10^7$  as distributing columns, and a refractometer was used as a detector. The molecular weight distribution of the polymer was measured at 40°C by using tetrahydrofuran (THF) as a developing solvent. The relative ratio of peak heights corresponding to the  
25 average molecular weights of branched polymer chains and unbranched polymer chains was calculated as the weight ratio of the respective polymer chains.

1 Solution viscosity

The viscosity of a solution having a polybutadiene concentration of 5% by weight in styrene monomer was measured by using a B-type rotating viscometer in a  
5 thermostat set at 25°C.

Referential Examples 1-3 & Comparative Referential  
Examples 1-5

By using the polybutadienes obtained in Examples 1-3 and Comparative Examples 1-5, 92 parts by weight of  
10 styrene monomer was added to 8 parts by weight of polybutadiene and the mixture was stirred and dissolved at room temperature. Then 0.08 part by weight of t-dodecylmercaptan was added and the mixture was stirred at 120°C for 4 hours to obtain a polymer solution in which about  
15 80% of styrene monomer was polymerized.

To 100 parts by weight of said polymer solution were added 150 parts by weight of water, 0.2 part by weight of aluminum hydroxide, 0.02 part by weight of sodium dodecylbenzenesulfonate, 0.3 part by weight of benzoyl  
20 peroxide and 0.05 part by weight of di-t-butyl peroxide, and the mixture was polymerized at 80°C for 4 hours, then at 100°C for 3 hours and finally at 130°C for 5 hours. From the produced polymer slurry, the polymer was filtered out, washed with water and dried to obtain a polystyrene  
25 resin.

Each of the thus obtained polystyrene resins, prepared as a specimen, was worked into a pressed sheet by

1 using an extruder and a compression molding machine,  
and subjected to a property evaluation. The results of  
evaluation are shown in Table 1.

The polybutadienes used in Referential Examples  
5 1-3 and Comparative Referential Examples 1-5 are those  
obtained in Examples 1-3 and Comparative Examples 1-5,  
respectively.

Izod impact strength was determined according to  
JIS K-6871, and surface luster was evaluated by visually  
10 observing the surface of each pressed sheet and scored  
according to the following 5-point system.

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Score	Surface condition
5	Having an extremely high smoothness and a high-degree luster like metallic luster. Very good.
4	Having a high smoothness and good luster.
3	Luster is observed but rather dim.
2	Surface appears hazy and has little luster.
1	Surface carries irregular patterns as if soil has deposited thereon and has little luster.

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Table 1

	Example	Comparative Example									
		1	2	3	4	5					
Polybutadiene	Amount used	n-butyllithium (millimoles)	8.2	9.5	8.7	11.0	17.5	12.0	7.2	5.0	
		Diethylene glycol dimethyl ether ( " )	0.74	1.0	1.1	-	0.65	2.0	0.7	0.8	
		Tin tetrachloride ( " )	1.3	2.3	1.9	2.8	4.2	3.0	0.5	-	
	Structural analytical values	Average 1,2-bond content (mol%)	20	25	28	9	14	40	20	25	
		1,2-bond content at starting end (H) (mol%)*	23	32	31	9	15	41	20	25	
		1,2-bond content at termination end (E) (mol%)*	19	23	26	9	13	40	20	25	
		[H] - [E] (mol%)	4	9	5	0	2	1	0	0	
		Mooney viscosity (ML, 1+4, 100°C)	60	65	72	96	46	78	65	60	
			Branched polymer chain content (%)	64	92	84	95	83	92	30	0
			Solution viscosity (5% styrene solution, 25°C)	75	61	67	95	30	75	120	140

- Cont'd -

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Table 1 (Cont'd)

	Referential example	Comparative referential example							
		1	2	3	4	5			
Properties	Izod impact strength (notched, kg.cm/cm)	12.2	10.9	11.8	9.5	7.6	6.5	7.9	8.1
	Surface luster	5	5	5	3	4	5	3	3
	Remarks	-	-	-	-	-	-	-	Stirring was difficult at the time of polystyrene polymerization.

\*1,2-bond contents at the starting end and termination end are respectively the calculated values of 1,2-bond contents in the 10% chain length portions.

## 1 Example 4

A polybutadiene was obtained by using the same autoclave and by following the same procedures of reaction and treatment as in Example 1.

5 In this example, however, the amounts of n-butyllithium, diethylene glycol dimethyl ether and tin tetrachloride used for the reaction were 8.7 millimoles, 1.0 millimole and 2.0 millimoles, respectively. Also, after starting the polymerization at 40°C, the poly-  
10 merization was continued while slowly increasing the temperature so that the temperature reached 50°C in 20 minutes and 70°C in 50 minutes, and after conducting the reaction at 70°C for 60 minutes, the reaction mixture was further reacted with tin tetrachloride. In the course  
15 of polymerization, a part of the polymerization solution was collected from the autoclave, and to this collected solution was immediately added methanol to stop the polymerization, and the resulting solution was used as a specimen for the determination of infrared absorption  
20 spectrum and polymerization conversion.

The 1,2-bond content in each chain length portion as calculated from the change of polymerization conversion and average 1,2-bond content are as shown in the following table.

Chain length from polymerization starting end/overall chain length	1,2-Bond content in each chain length portion (mol%)	Average 1,2-bond content (mol%)
0 - 10%	32	26
10 - 90%	25	
90 - 100%	23	

- 1            This polybutadiene also showed the following results of determination: Mooney viscosity at 100°C = 72; solution viscosity (5% polybutadiene solution in styrene at 25°C) = 66 cps; branched polymer chain content = 85%.

#### 5   Referential Example 4

          By using the polybutadiene obtained in Example 4, an impact-resistant polystyrene was synthesized according to the procedure of Referential Example 1. This polystyrene showed an Izod impact strength of 13.2 kg·cm/cm and had a score of 5 on surface luster evaluation, indicating a good balance of improved properties.

#### Comparative Referential Example 6

          A polystyrene resin was obtained by following the same procedure as Referential Example 1 but by using a commercial polybutadiene having an average 1,2-bond content of 13% by mole, a Mooney viscosity of 37 and a solution viscosity of 83 cps. This resin had an Izod impact strength of 9.6 kg·cm/cm and a score of 3 on the surface

1 luster evaluation.

WHAT IS CLAIMED IS:

1. A polybutadiene having branched polymer chains obtained by polymerizing 1,3-butadiene in the presence of an organolithium compound and a Lewis basic compound and further reacting the resulting polymer with a polyfunctional halogen compound, said polybutadiene having an average 1,2-bond content of 18 to 32% by mole, a branched polymer chain content of 60% by weight or more and a Mooney viscosity at 100°C of 40 to 90, and the viscosity of a 5% by weight concentration solution of the polybutadiene in styrene at 25°C being 60 to 90 cps.
2. A polybutadiene according to Claim 1, having its 1,2-bond content distribution along the lengthwise direction of polymer chains, the 1,2-bond content (% by mole) in the portion of 10% chain length from the polymerization starting end being 3 to 20% by mole greater than the 1,2-bond content (% by mole) in the 10% chain length portion from the polymerization termination end.
3. A polybutadiene according to Claim 1 or 2, having an average 1,2-bond content of 20 to 30% by mole.
4. A polybutadiene according to Claim 1 or 2, having a branched polymer chain content of 80% by weight or more.
5. A polybutadiene according to Claim 3, having a branched polymer chain content of 80% by weight or more.
6. A process for producing a polybutadiene having branched polymer chains, said polybutadiene having an average 1,2-bond content of 18 to 32% by mole, a branched

polymer chain content of 60% by weight more and a Mooney viscosity at 100°C of 40 to 90, the viscosity of a 5% by weight concentration solution of the polybutadiene in styrene at 25°C being 60 to 90 cps, said process comprising starting the polymerization of 1,3-butadiene in an inert hydrocarbon solvent in the presence of a Lewis basic compound and an organolithium compound in an amount of 0.5 to 3 millimoles per 100 g of 1,3-butadiene at a temperature selected from the range of 30 to 80°C, conducting the polymerization while controlling the temperature so that the temperature at the end of the polymerization may be 5 to 40°C higher than the temperature at the start of the polymerization, and adding to the resulting polymer solution a polyfunctional halogen compound in an amount of 0.6 to 1 equivalent per equivalent of the organolithium compound to effect further reaction thereof.

7. A process according to Claim 6, wherein the Lewis basic compound is selected from the group consisting of ethers such as diethyl ether, dibutyl ether, tetrahydrofuran, ethylene glycol dimethyl ether, ethylene glycol dibutyl ether, diethylene glycol dimethyl ether, diethylene glycol dibutyl ether and the like, and tertiary amines such as triethylamine, tributylamine, N,N,N',N'-tetramethylethylenediamine and the like.

8. A process according to Claim 7, wherein the Lewis basic compound is diethylene glycol dimethyl ether.

9. A process according to Claim 6 or 7, wherein

the organolithium compound is selected from hydrocarbon compounds containing lithium atom such as n-propyllithium, isopropyllithium, n-butyllithium, sec-butyllithium, t-butyllithium, n-pentyllithium and the like.

10. A process according to Claim 9, wherein the organolithium compound is n-butyllithium.

11. A process according to Claim 6 or 7, wherein the polyfunctional halogen compound is selected from the group consisting of dimethylsilicon dichloride, monomethylsilicon trichloride, silicon tetrachloride, tin tetrachloride and germanium tetrachloride.

12. A process according to Claim 11, wherein the polyfunctional halogen compound is tin tetrachloride.

13. A process according to Claim 9, wherein the polyfunctional halogen compound is selected from the group consisting of dimethylsilicon dichloride, monomethylsilicon trichloride, silicon tetrachloride, tin tetrachloride and germanium tetrachloride.

14. A process according to Claim 13, wherein the polyfunctional halogen compound is tin tetrachloride.

